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(54) Process for the Production of Titanium Dioxide

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A process the production of titanium dioxide

Abstract of the Disclosure

The present invention relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag.

A process for the production of titanium dioxide

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10 The present invention relates to a process for the  
production of titanium dioxide by discontinuous digestion  
of titanium slag with sulphuric acid, production of a  
titanyl sulphate solution suitable for hydrolysis from the  
solid digestion cake obtained during digestion, hydrolysis  
15 of the titanyl sulphate, separation and calcination of the  
titanium-containing hydrolyzate, evaporation of the waste  
acid separated from the hydrolyzate and re-use of the  
sulphuric acid separated from the evaporated waste acid  
in the digestion of titanium slag.

20 The requirement for recycling of sulphuric acid from  
the  $TiO_2$  production process by the sulphate process is  
having to be met more and more. In addition to the  
expected economic disadvantages in comparison with dumping  
of waste acid in the ocean, the process often encounters  
technical problems.

25 A process for working up waste acids is known from  
DE-A 3 327 769 and is adopted on an industrial scale. De-  
pending on the local condition, however, problems can  
arise here if the waste acid is to be almost completely  
recycled.

30 According to the working up process currently  
adopted, the waste acid is concentrated, preferably by  
multi-stage vacuum evaporation, until a 60 to 70%  
sulphuric acid with a low content of dissolved metal  
sulphates can be separated by filtration from crystal-  
lized metal sulphates.

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5       The concentration of this recovered sulphuric acid  
is generally too low, however, to produce a sulphuric acid  
initial concentration suitable for the discontinuous  
digestion of raw material when mixed with fresh sulphuric  
acid or oleum, which is required for replacing the sul-  
phuric acid losses (by metal sulphate binding, residual  
10       moisture in the separated metal sulphates, waste water).  
It is therefore necessary further to evaporate the sul-  
phuric acid separated from the metal sulphates, and this  
can be effected, for example, by using the waste heat from  
TiO<sub>2</sub> calcination (EP-A 97 259).

15       The greater the content of recycled sulphuric acid  
in the total mixture, the higher the concentration of the  
recycled acid must be. As the concentration increases,  
however, the requirements in energy and equipment also  
increase. In particular, when using the titanium slags  
20       which are advantageous from an ecological point of view  
as raw material, a particularly high concentration of the  
recycled acid is required if maximum possible industrial  
recycling is desired.

25       A more desirable situation arises if the relatively  
low sulphuric acid losses during digestion of the titanium  
slags can be replaced by 95 to 98% sulphuric acid ("fresh  
acid") instead of oleum. The production of oleum can thus  
be omitted.

30       In this case, according to the prior art it is only  
possible to concentrate recycling acid in a high concen-  
tration apparatus (for example a Pauling distillation  
vessel) to about 96% (Ullmanns Encyklopädie d. techn.  
Chemie, 4th edition, volume 18, page 579, Verlag Chemie,  
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5 Weinheim 1979). However, this stage of the process is extremely expensive with respect both to the investment costs and to the energy and maintenance costs.

It is accordingly the object of the present invention to propose a method which overcomes the above-mentioned disadvantages of the prior art in an economical manner.

10 This object can surprisingly be achieved by the following combination of measures:

- evaporation of the 60 to 75% sulphuric acid separated from the metal sulphates and containing dissolved metal sulphates under vacuum in horizontal or circulation evaporators at from 120 to 190°C to 76 to 87%  $H_2SO_4$  (based on salt-free sulphuric acid),
- 15 mixing of the ground titanium slag with 95 to 98% sulphuric acid at from 30 to 80°C and addition of the recycled acid at a temperature of from 80 to 190°C, preferably from 100 to 160°C.

The present invention accordingly relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, 25 evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in titanium slag digestion, a 60 to 75% pre-concentrated sulphuric acid being separated from the solid metal sulphates and hydrogen sulphates after

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5 evaporation of the waste acid, this sulphuric acid being further evaporated under vacuum to a concentration of between 76 to 87%  $H_2SO_4$  (calculated as salt-free sulphuric acid) and being used together with 95 to 98% sulphuric acid in the digestion of the ground titanium slag.

10 The invention also teaches the conditions under which the titanium slag is to be digested in order to keep the necessary concentration of the recycled sulphuric acid and therefore the costs of sulphuric acid concentration as low as possible.

15 The titanium slag is advantageously mixed with warm 95 to 98% sulphuric acid ("fresh acid") at from 30 to 80°C, preferably from 50 to 80°C.

20 Digestion is initiated by addition of the uncooled or slightly cooled recycled acid, supplied from sulphuric acid evaporation to the warm fresh acid/slag mixture. The process corresponding to the prior art involving initiating digestion by addition of water or introduction of steam would require a substantially higher concentration of the recycled acid than the process according to the invention.

25 A particularly preferred embodiment of the process according to the invention therefore involves initiating the digestion reaction by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 80 to 190°C, preferably from 100 to 160°C.

30 A further reduction in the minimum sulphuric acid concentration required for discontinuous slag digestion by 2 to 3%, without losses of  $TiO_2$  yield occurring, is successful because steam is blown through the digestion cake instead of air during the maturing time once the  
35 maximum reaction temperature has been reached.

5 In a particularly desirable embodiment of the process according to the invention, the concentration of the sulphuric acid is advantageously between 87 and 91%, preferably 88 and 90%  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the start of the digestion reaction and  
10 from 35 to 70% of the required sulphuric acid is recovered as recycled acid from the process.

The necessary temperatures of the fresh acid and the recycled acid can be lowered according to the invention by grinding the titanium slag more finely.

15 The production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is preferably carried out by evaporation at from 120 to 190°C and from 40 to 150 mbar.

20 Horizontal evaporators with tantalum heat exchangers or circulation evaporators are particularly suitable for these evaporation processes not only for reasons of energy consumption.

25 Valuation of the process according to the invention has to consider the fact that secondary energy can be used instead of primary energy for producing the recycled acid and that the investment and maintenance costs are substantially lower compared with the prior art.

The drawing serves to illustrate the process according to the invention.

30 The fresh acid (1) required for the digestion of raw material is mixed in the digestion reactor (3) or in a preceding mixer with the ground titanium slag (2) (optionally with addition of ground ilmenite). The fresh acid should have a temperature of from 30 to 80°C,  
35 preferably from 50 to 80°C. The necessary quantity of

5 recycled acid (17) is introduced at a temperature of from  
80 to 190°C, preferably from 100 to 160°C, into the  
digestion reactor (3) while blowing air through the  
mixture present and the exothermal reaction is thus  
initiated. If steam (4) which is at least 150°C hot is  
10 blown in instead of air once the maximum reaction temper-  
ature has been attained, the temperature drop of the  
digestion mixture can be reduced and the  $TiO_2$  yield  
improved. After a maturing time of from 5 to 8 hours,  
after which, from experience, no further improvement in  
the  $TiO_2$  yield can be expected, the digestion cake is  
15 dissolved with water or preferably with sulphuric acid-  
containing waste water (5) from the  $TiO(OH)_2$  hydrolyzate  
filtration process.

The titanyl sulphate solution is prepared in known  
manner for hydrolysis. During the hydrolysis process (6),  
20 sulphuric acid-containing waste water (5) is preferably  
used as diluent water. The hydrolyzate (8) is calcined in  
known manner to titanium dioxide (10).

The metal sulphate-containing sulphuric acid (waste  
acid) (11) produced during filtration (7) normally has a  
25 concentration of from 20 to 27%  $H_2SO_4$ . It can be pre-  
evaporated using process heat before being evaporated in  
known manner in an evaporator which is preferably a  
multistage vacuum evaporator (12) until most of the metal  
sulphates are crystallized and a 60 to 75% sulphuric acid  
30 remains (= evaporation 1).

After cooling the suspension supplied from the  
evaporation I to from 40 to 70°, the metal sulphates (14)  
are separated from the sulphuric acid, preferably by  
35 filtration (13).



5 The metal sulphates are partly in the form of  
hydrogen sulphates and contain 60 to 75% sulphuric acid  
as moisture. It is therefore advantageous to decompose  
this "filter salt" thermally with formation of  $\text{SO}_2$  and to  
10 produce therefrom the 95 to 98% sulphuric acid required  
as fresh acid. However, reaction with Ca compounds (DE-A  
3 327 770) or a different harmless elimination process is  
also possible.

Sulphuric acid losses occur mainly through the filter  
salt, but also through the moisture of the solid residues  
15 resulting from raw material digestion, the sulphuric acid  
bound in the  $\text{TiO}(\text{OH})_2$  and the unavoidable waste water. As  
pre-concentrated acid, therefore, only about 40 to 60% of  
the sulphuric acid used during digestion can be recovered.  
With 60 to 75%  $\text{H}_2\text{SO}_4$ , however, the concentration of this  
20 acid is too low to allow autothermal slag digestion in  
mixture with the necessary amount of from 95 to 98% fresh  
acid.

The pre-concentrated acid (15) which still contains  
about 3 to 6% by weight of dissolved metal sulphates  
therefore must be evaporated in an evaporation II (16) to  
25 76 to 87%  $\text{H}_2\text{SO}_4$  (as salt-free acid), before it can be  
recycled (17) for the digestion of the raw material. The  
evaporation II (16) is carried out according to the inven-  
tion by vacuum evaporation at 120 to 190°C. Circulation  
evaporators or horizontal evaporators with tantalum heat  
30 exchangers can be used as evaporator systems. Horizontal  
evaporators are preferred owing to the particularly high  
specific evaporation capacity (with respect to the  
tantalum heat exchanger surface). Preheating of the pre-

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5 concentrated sulphuric acid almost to boiling point is  
advantageous (at a given evaporation pressure). Steam-  
heated graphite heat exchangers are preferred for the  
preheating operation. Cooling of the recycled acid  
supplied from the evaporator is omitted or is optionally  
10 carried out using the pre-concentrated acid introduced as  
a cooling liquid, only until the temperature of the  
recycled acid is still sufficient to initiate the di-  
gestion reaction in the manner described above, i.e. until  
the temperature lies in the range of from 80 to 190°C.

15 A substantial advantage of the process according to  
the invention lies in the fact that problems which arise  
during further cooling of this acid are avoided by using  
the recycled acid at a temperature of from 80 to 190°C  
because the metal sulphates dissolved in that acid (about  
4 to 7% by weight) crystallize in an extremely finely  
20 divided form at lower temperatures. As these salts tend  
to settle on cool surfaces, they lead to frequent inter-  
ruptions in the operation. These problems can be avoided  
by introducing the recycled acid at a temperature at which  
the dissolved metal sulphates not yet crystallize.

25 The process according to the invention, which is  
substantially more economical than conventional high  
concentration processes according to the prior art  
evaporating sulphuric acid to about 96%  $H_2SO_4$  and  
initiating the digestion reaction by introduction of  
30 steam into the sulphuric acid-slag mixture will be  
described with reference to the following non-limiting  
Examples.

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Example 1 (Comparison Example)

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17.5 t of ground titanium slag were mixed with 18 t of metal sulphate-containing recycled acid and with 13.6 t of fresh 96% sulphuric acid (20°C). The digestion reaction was initiated by addition of 1.4 t of water and introduction of 0.6 t of steam. The maximum reaction temperature of 203°C was attained after 10 minutes. After initiation of the reaction, air was blown through the mixture (for 30 minutes at 350 m<sup>3</sup><sub>n</sub>/h, then for 7 hours at 20 m<sup>3</sup><sub>n</sub>/h). After a maturing time of 7 hours, the digestion cake had a temperature of 169°C. The TiO<sub>2</sub> yield was 95.3%.

The digestion cake was dissolved with a proportion of the sulphuric acid-containing waste water from the hydrolyzate filtration (5.4% by weight H<sub>2</sub>SO<sub>4</sub>). After working up the titanyl sulphate solution, the mixture was hydrolysed using a further proportion of the sulphuric acid-containing waste water as diluent water.

85 t of waste acid containing 23.2% H<sub>2</sub>SO<sub>4</sub> and 29.8% SO<sub>4</sub><sup>2-</sup> (total) were separated from the hydrolyzate filtration process. The waste acid was evaporated in a 2-stage vacuum evaporator until the sulphuric acid (calculated as salt-free acid) had a concentration of 66% H<sub>2</sub>SO<sub>4</sub>. 31 t of 5 bar steam were used up for evaporating 47.5 t of H<sub>2</sub>O.

11.3 t of sulphuric acid-containing filter cake were separated from the metal sulphate-sulphuric acid suspension after cooling to 55°C. The pre-concentrated acid (25.7 t) contained 62.8% of H<sub>2</sub>SO<sub>4</sub>, 32.4% of H<sub>2</sub>O and 4.8% of dissolved metal sulphates.

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5 introduced had a temperature of  $89^{\circ}\text{C}$  and the discharged  
recycled acid had a temperature of  $145^{\circ}\text{C}$ . Only 4.94 t of  
10  $\text{H}_2\text{O}$  had to be evaporated instead of 5.7 t of  $\text{H}_2\text{O}$ . The  
total energy consumption for the production of the  
recycled acid from pre-concentrated acid and the blowing  
of steam through the digestion cake was 19,460 kJ in  
comparison with 22,700 kJ in Example 2.

#### Example 4

15 Laboratory experiments were carried out to examine  
how the temperature of the recycled acid can be lowered  
without problems arising due to an excessively slow rate  
of the digestion reaction. 500 g of slag ground to varying  
finenesses were mixed with 520 g of 96% sulphuric acid and  
preheated to the temperature  $T_1$ . The mixture was then  
20 mixed in an insulated vessel with 590 g of pure 85% sul-  
phuric acid having a temperature of  $T_2$ . The mixture was  
stirred while introducing 250 l of air/h and the temper-  
ature gradient was recorded. The experimental results are  
compiled in Table 1.  $T_3$  is the temperature of the mixture  
25 after addition of the 85% sulphuric acid and  $T_4$  the  
maximum temperature attained.  $t$  is the time period until  
the maximum temperature is attained after addition of the  
85% acid.

Table 1

5

Exp. No.	Fineness of grinding % by weight <40 $\mu$ m	T <sub>1</sub> [°C]	T <sub>2</sub> [°C]	T <sub>3</sub> [°C]	T <sub>4</sub> [°C]	t [min]
10	1	81	50	110	76	-
	2	81	50	140	91	106
	3	81	70	140	101	154
	4	81	80	140	109	193
	5	81	70	160	117	192
	6	100	50	120	86	168
15	7	100	50	140	95	185
						28

20 The experimental results show that the temperature of the recycled acid can be lower if the titanium slag is ground more finely (Experiment 7) than with a coarser grinding (Experiment 2) achieving approximately the same reaction rate. Also the temperature of the 96% fresh acid can obviously be lowered instead of the temperature of the recycled acid.

25 The slower rise in the temperature of the laboratory digestions in comparison with the rise in temperature on an industrial scale is due to the relatively high thermal losses.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, the production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag, characterized in that, after evaporation of the waste acid from the solid metal sulphates and hydrogen sulphates, a 60 to 75% pre-concentrated sulphuric acid is separated and is further evaporated under vacuum to a concentration of between 76 and 87%  $H_2SO_4$  (calculated as salt-free sulphuric acid) and is used together with 95 to 98% sulphuric acid in the digestion of the ground titanium slag.
2. A process according to claim 1, wherein the titanium slag is mixed with warm 95 to 98% sulphuric acid ("fresh acid") at from 30 to 80°C.
3. A process according to claim 2, wherein the fresh acid is mixed at from 50 to 80°C.
4. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 80 to 190°C.

5. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76 to 87% sulphuric acid ("recycled acid") at from 100 to 160°C.
6. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 87 and 91%,  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
7. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 88 and 90%  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
8. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar.
9. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a horizontal evaporator with a tantalum heat exchanger is used as evaporator.
10. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric

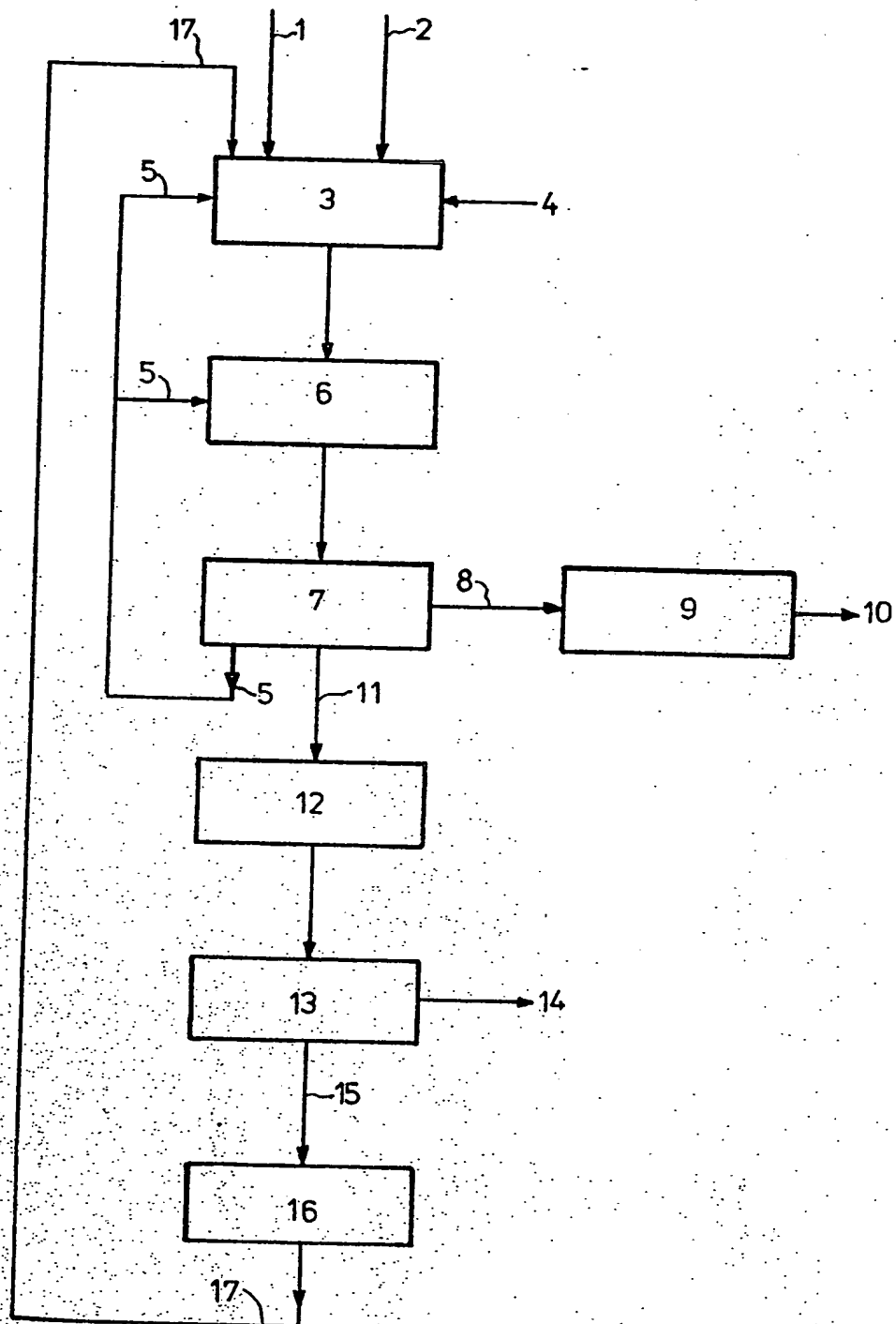
acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a circulation evaporator is used as evaporator.

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